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## HIGH TEMPERATURE OXIDATION OF PROPARE

N. Ya. Chernyak and V. Ya. Shtern Moscow State U imeni M. V. Lomonosov Submitted by Acad N. N. Semenov, 2 March 1951

Figure and tables referred to are appended.

The oxidation of propens was studied under static conditions for the mixture C3H3 + O2 at T-350° and P initial = 282 mm of mercury; i.e., in that region of high temperature oxidation in which the negative temperature coefficient of the reaction velocity is clearly expressed. Employment of analytical methods gave us the possibility of quantitively determining the following possible components of the reacting mixture: C3H8, O2, C3H6, C2H4, CH4, C3H6, H2, CO, CO2, HCHO, CH3CHO, CH3OH, the sum of higher alcohols, the sum of scids, E202, and organic peroxide. Separate determination of HCHO and CH\_CHO was insured by use of the polargraphic method of analysis; for separate determination of CF30H and the sum of higher alcohols, the method of cridizing with a mixture of K<sub>2</sub>Cr<sub>2</sub>O+H<sub>2</sub>SO<sub>1</sub>, was used (with a preliminary asparation of alcohols from other products); for the determination of saturated hydrocarbons a method of low temperature evaporation at low pressure was used. the arount of water formed during the oxidation was calculated by the difference between the spent quantity of E2 (from C3H2) and O2, and their amount found in the formed intermediated and end products. Since the ratio between the differences (H2: 02) cal mated by this means was always close to two, the amount in quantion was assumed to represent water only.

The kinetics of expenditure of initial products and accumulation of intermediate and end products of exidation in mixture C3H8+02 under the selected conditions (T=350° and  $P_{initial}$  282 mm), as well as the kinetics of this reaction under pressure are set forth in Figure 1. As seen from the drawing, the

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quantities of peroxiles (principally  $\rm H_2O_2$ ) and aldehydes (HCHO\_and CH\_2UHO) reach, with a maximum total increment of pressure amounting to  $\rm Ap=30~ms$ , certain maximum values (1.8 : 11.5 and 4.5 mm, respectively), after which the concentration of peroxiles begins to decrease (to 0.2 mm towards the end of the interaction), while the concentration of aldehydes remains constant. Semilogarithmic annuarphosis of the concentration curves of the peroxides and aldehydes gives straight lines to the points where these intermediate products reach maximum concentrations. This proves that accumulation takes place according to an exponential law. As for as alcohole are concerned, only withyl alcohol is obtained in the oxidation of propens. Its quantity increases throughout the entire run of the reaction, reaching at the ond a value of 25 mm.

Propylene and ethylene accumulate during the entire run of the oxidation, reaching at its end 19 and 8 km, respectively. Throughout the extent of the entire reaction the relationship  $c_3H_6$ :  $c_2H_b{\approx}2.3$ . Methane is found in the products of the reaction in quantities of the same order as the quantity of ethylene.

A fact worth noting is that the ratio of the emount of propane used for the formation of exygen-containing products --  $\mathrm{CH_3OH}$ ,  $\mathrm{HCHO}$ ,  $\mathrm{OH_3CHO}$ , exygen, CO, CO, to its amount used for the formation of  $\mathrm{C_3H_6}$ ,  $\mathrm{C_2H_6}$  and  $\mathrm{CH_6}$ , increases during the run of the reaction (from 0.6 at p=10 rm to 1.17 at p=60 m). This fact must be considered in drawing up the scheme of the process.

A full balance on  $C_3H_2$  and  $C_0$  for the entire run of the reaction is set forth in Table 1, from which it follows that the analysis covers all the main products of the oxidation. The ratio of formed water, determined by calculation from the balance, to the total amount of  $CO+CO_2$  remains constant during the run of the reaction and is nearly equal to 1.4.

Calculation of the reaction rate from the increment in total pressure and consumption of  $O_2$  shows that the maximum rate of consumption of  $O_2$  occurs at the maximum, while the maximum rate of peroxide and aldehydes reach their maximum, while the maximum rate of increase in total pressure takes place such earlier ( p 17 mm). In this is found one of the kinetic manifestations of the difference between the processes of oxidation of  $O_3H_6$  and  $O_3H_6$ .

The influence of adding CH<sub>3</sub>CHO, C<sub>3</sub>H<sub>6</sub> and CH<sub>3</sub>CH on the exidation of the mixture C<sub>3</sub>H<sub>6</sub>+O<sub>2</sub> at T=350° and P initial 282 mm was studied. This proved that adding 1.9 mm CH<sub>3</sub>CHO (i.e., two and one half times less than its maximum accumulation in the reaction) shortens the time required for reaching the maximum rate by a factor of 8 and dcubles the absolute value of the latter. The quantities of RCHO and CH<sub>3</sub> CHO found at the end of the reaction (even when adding eight mm CH<sub>3</sub>CHO to the initial mixture) remain the same as they would without any addition of CH<sub>3</sub>CHO. Adding C<sub>3</sub>H<sub>6</sub> and CH<sub>3</sub>OH to the original mixture effected an increase in final yield of these substances equal approximately to the smount added. From this it follows that C<sub>3</sub>H<sub>6</sub> and CH<sub>3</sub>OH formed during the exidation are not subject to further exidation under our conditions.

In experiments on prepared mixtures analogous to those which were described for the oxidation of  $C_3R_6$  (2), it was found that in the case of  $C_3R_8$ , the substance which determines the branched-degenerate character of the oxidation is also  $CR_3CEO$ .

The course of the oxidation of propene was determined by considering the following:



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- a). The wridetion of propose does not take place through the oridation of C3E6 formed in the course of the reaction. This is indicated by the result of experiments in which C3H6 was added to the initial mixture (see above).
- b) C3H6, C2H6, CH4 and H2, the usual products of propane cracking, are also obtained by cracking in its oxidation. The fact that in the case of exidation these products are formed at scannial lower temperatures, is explained by the presence of C2, which noticeably facilitates the course of the reaction along the path of cracking.
- c) HUHO, formed in the resetion, is not a product of the degradation of CH3 CNO. This follows from the absence of any influence of addition of CH3CH0 to the initial mixture on the amount of HCHO found at the end of the reaction (see above).
- c) Further oxidation of the aldehydes formed in the reaction proceeds according to the summary equations:  $HCHO+\frac{1}{2}O_2=CO+H_2$ 0 and  $CH_3CHO+\frac{1}{2}O_2=2CO+L_2O$ 0. By the same course of oxidation of aldehydes,  $CO_2$  is obtained and, just like  $CO_2$  is obtained in equimolecular quantities with the water formed at the same time.
- e) Water is formed not only in the oxidation of aldehydes. This follows from the fact that the relationship of  $H_20:(C0+CO_2)>1(\cong 1.4$  throughout the entire run of the reaction).

0) 
$$c_3 E_8 + 0_2 = (n + 1so) c_3 E_7 + 40_2$$

5) 
$$1-C_3H_7+O_2=1-C_3H_7O_2$$

8) 
$$n-c_3H_7+c_2=n-c_3H_7c_2$$



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- 13) 20H3CHO+02=2СH3COOH
- 14) CH3COCH+0,=200+2H30
- 15) 20H20+02=200+2H20
- 16) n-C3H702-> break
- 17) 1-c<sub>5</sub>70<sub>2</sub>-> break

The scheme postulates two directions of the reaction, cracking and oxidation. The first is brought about by the decomposition of n-C<sub>3</sub>H<sub>7</sub> only, the second by the oxidation of n-C<sub>3</sub>H<sub>7</sub> as well as i-C<sub>3</sub>H<sub>7</sub>. In this connection it is assumed that the free radicals and atoms arising from the decomposition and oxidation of n-C<sub>3</sub>H<sub>7</sub> (i.e., CH<sub>3</sub>, H, OH) are sufficiently active for regeneration of n-C<sub>3</sub>H<sub>7</sub> during the reaction starting with the initial propane, while the radicals formed by way of oxidation of 1-C<sub>3</sub>H<sub>7</sub> and in the course of oxidation of CH<sub>3</sub>CHO leading to branching (i.e., to CH<sub>3</sub>O and CH<sub>2</sub>CHO), by virtue of their weaker activities are capable of regenerating i-C<sub>3</sub>H<sub>7</sub> only (in the reaction starting with propane). In this manner, the branched part of the oxidation path of the reaction turns out to be fully separated from the cracking. This makes it possible to explain the observed growth, during the course of the process, of the ratio of C<sub>3</sub>H<sub>8</sub> used up in the oxidation, to C<sub>3</sub>H<sub>8</sub> used up in cracking (see above).

Out of the scheme and the assumed conditions the following relations follow:

- 1. The emounts of actually formed (i.e., without taking into consideration further oridation) CH<sub>3</sub>OH and CH<sub>3</sub>CHO must be equal to each other.
- 2. The amount of  $H_{20}$  obtained other than by oxidation of aldehydes, i.e.,  $/\bar{H}_{20} (CO + CO_2)$  must equal one third of the actually formed RCHO.
- 3. Lowering of the concentration of 0, during the course of the reaction must be reflected in an increase of the ratio of actually formed CH<sub>3</sub>CHO to HCHO.

In checking these relationships, it is necessary to calculate the amount of actually formed ECHO and CH<sub>3</sub>CHO at every given moment of the reaction. This can be done in the following way. Since the formed CH<sub>3</sub>CH does not undergo further oxidation, its analytically determined amount is equal to the amount of actually formed CH<sub>3</sub>CHO (prior to the latter's conversion). The difference between the CH<sub>3</sub>CHO determined in this manner and the analytically determined CH<sub>3</sub>CHO gives the amount of CH<sub>3</sub>CHO subjected to oxidation. Subtracting from the analytically found sum of  $(CO+CO_2)$  twice the amount of oxidized CH<sub>3</sub>CHO, we get the amount of  $(CO+CO_2)$  formed through the oxidation of ECHO. Adding it to the analytically determined amount of ECHO, we find the amount of actually formed HCHO.

Calculating in this manner the amounts of CH<sub>2</sub>CHO and ECHO actually formed in the course of the reaction, one may compare one third of the virtually formed HCHO with the experimentally obtained difference  $/\mathbb{H}_2O+(CO+CO_2)$  and compute the ratio of CH<sub>3</sub>CHO to HCHO. As seen by the values in Table II, this gives a good confirmation of the relationships derived from the proposed scheme.



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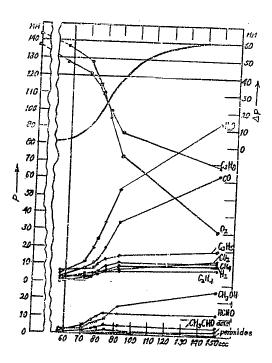


Fig. 1. Oxidation in Propane-Oxygen Mixture.



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Table 1

318402; T=3500, Pinitial = 232 wn Hg

Prossure	Time Nixture in Vessel (sec)	<u> </u>		<b>H</b> <sub>2</sub> √							
Increment (pm)		Expended	Found	Expended	Found	Difference	Expended.	O <sub>2</sub>	Difference	H <sub>2</sub> O by Residual	
3 10 17 22 30 40	57 71.5 76.5 79.2 84 92.5	30 51 72 87 117 153 210	31.4 51.5 70.2 84.6 115.4 156 208.2	40 68 96 116 160 204 260	34.2 52 71.8 90.6 114 148.5 180.5	5.8 16 24.2 25.4 46 55.5	6.7 16 29 31: 48.3 70.6	4.45 10 19.2 21.8 31 43.5	2.25 6 9.8 12.2 17.3 27.1	4.5 12 20 24.4 34.6 54.2	

Table 2

	HIXTURE CH	3-0 <sub>2</sub> ; T=3500; P	- 280	nim 77_		
Pressure increment (mm)	3.0	17		en ug		
One third of actually formed of HCHO in mm (calculated)		-1	22	30	40	60
Æ,0 - (co+co₂) 7 tn	3.56	5-55	6.9	9.7	10.6	15.8
Ratio of actualia	3.4	5.2	6.9	8.9	11.3	16.7
formed CH3CEO : ECHO	0.215	0,33	0.32	0.30	0.49	0.5h

